

Scientific Report
Oct. 2013– Dec. 2014

New metal complexes with metal-chalcogen bonds - potential precursors for electronic materials. code PN-II-ID-PCE_2011-3-0659

Objectives accomplished during the period Oct. 2013 – Dec. 2014

- Design of new organo-chalcogen ligands.
- Synthesis of new compounds derived from the hypervalent diorganodiselenides [2,6-(R₂NCH₂)C₆H₃]₂Se₂ (R = Me, R₂ = O(CH₂CH₂)₂, MeN(CH₂CH₂)₂).
- New organometallic compounds of main group metals (Sb, Bi or Sn) with organo-chalcogen ligands.
- New complexes of *d* - metals with organo-chalcogen-, alkoxo or carboxilato ligands.
- Thermal behavior of the new precursors.
- Final characterization of several compounds obtained in 2012 and 2013.

In Table 1 are depicted the obtained compounds along with several analytical data.

- All new compounds were characterized by multinuclear NMR (¹H, ¹³C, ³¹P, ⁷⁷Se, as appropriate) and mass spectrometry, and part of them by IR spectroscopy or single-crystal X-ray diffraction.

Majority of the reactions were performed under argon atmosphere, using dried and freshly distilled solvents.

Table 1

Nr.	Compound	m.p. °C	η, %	Color	⁷⁷ Se NMR [ppm]
1	[2-(Me ₂ NCH ₂)C ₆ H ₄]Se[CH ₂ CH ₂ pz]	92	68	yellow	455.1
2	[2-(Me ₂ NCH ₂)C ₆ H ₄]S[CH ₂ CH ₂ pz]	85	71	yellow	-
3	Se(CH ₂ CH ₂ pz) ₂	87	74	yellow	409.4s
4	S(CH ₂ CH ₂ pz) ₂	101	82	yellow	-
5	{[2-(Me ₂ NCH ₂)C ₆ H ₄]Se[CH ₂ CH ₂ pz]}AgOTf	124	78	colorless	124.5
6	{[2-(Me ₂ NCH ₂)C ₆ H ₄]S[CH ₂ CH ₂ pz]}AgOTf	107	81	beige	-
7	[Se(CH ₂ CH ₂ pz) ₂]AgOTf	152	68	beige	163.7
8	[S(CH ₂ CH ₂ pz) ₂]AgOTf	134	74	colorless	-
9	[2,6-{MeN(CH ₂ CH ₂) ₂ NCH ₂ }C ₆ H ₃]Se ₂	94	82	orange	-
10	[2,6-{MeN(CH ₂ CH ₂) ₂ NCH ₂ }C ₆ H ₃]SeCl	187	68	yellow	921.4
11	[2,6-{O(CH ₂ CH ₂) ₂ NCH ₂ }C ₆ H ₃]SeCl	175	73	colorless	1007.3

12	[2,6-(Me ₂ NCH ₂)C ₆ H ₃]SeCl	138	65	orange	972.3
13	[2,6-(Me ₂ NCH ₂)C ₆ H ₃]SeAgOTf	143d	83	colorless	128.7
14	[2,6-(Me ₂ NCH ₂)C ₆ H ₃]SeAuCl	111d	74	brown	134.6
15	[PhO(C ₆ H ₄) ₂ Se ₂	84	48	orange	355.6
16	[PhO(C ₆ H ₄) ₂ S ₂	71	62	yellow	
17	[PhO(C ₆ H ₄) ₂ Te ₂	95	46	red	210.45 ^a
18	[(C ₆ H ₄ CH ₂) ₂ S]BiBr	190	67	yellow	-
19	[(C ₆ H ₄ CH ₂) ₂ S]BiI	178	98	yellow	-
20	[(C ₆ H ₄ CH ₂) ₂ S]BiONO ₂	150	88	colorless	-
21	[2-(Me ₂ NCH ₂)C ₆ H ₄] ₂ Sn(NCSe) ₂	187	81	colorless	76.31s
22	[2-(Me ₂ NCH ₂)C ₆ H ₄] ₂ Sn(NCS) ₂	248	90	colorless	-
23	[2-(Me ₂ NCH ₂)C ₆ H ₄]Bu ⁿ Sn(NCS) ₂	110	64	colorless	-
24	[2-(Me ₂ NCH ₂)C ₆ H ₄]Bu ⁿ Sn(S ₂ CNMe ₂) ₂	97	78	colorless	-
25	[2-(Me ₂ NCH ₂)C ₆ H ₄] ₂ Sn(S ₂ CNMe ₂) ₂	114	92	colorless	-
26	{[Me ₂ C(O)CH ₂][C ₆ H ₄ CH ₂ NMe ₂]Se} ₂ Sn[N(SiMe ₃) ₂]	-	56	colorless	227
27	{[Me ₂ C(O)CH ₂][C ₆ H ₄ CH ₂ NMe ₂]S} ₂ Sn[N(SiMe ₃) ₂]	-	43	colorless	-
28	{[C ₆ H ₄ CH ₂ NMe ₂] ₂ S} ₂ Sn[N(SiMe ₃) ₂]	-	74	yellow	-
29	{[C ₆ H ₄ CH ₂ NMe ₂] ₂ Se} ₂ Sn[N(SiMe ₃) ₂]	-	84	yellow	188
30	[2-(Me ₂ NCH ₂)C ₆ H ₄]SeCdCl	135	51	yellowish	-81
31	[2-(Me ₂ NCH ₂)C ₆ H ₄]SCdCl	169	77	yellowish	
32	(4-MeC ₆ H ₄)SeCdCl	97	58	yellowish	-102
33	[2-(Me ₂ NCH ₂)C ₆ H ₄]SeCd[(SPPH ₂)(OPPh ₂)N]	123	64	yellowish	-52,7
34	[2-(Me ₂ NCH ₂)C ₆ H ₄]SeCd[(SePPh ₂) ₂ N]	141	52	yellowish	-43,8, larg
35	(3 <i>H</i> -2-thioxo-1,3,4-thiadiazol-5-yl)-thiosuccinic acid	123	93	yellowish	-
36	(C ₂ N ₂ S ₃ CH(COO)CH ₂ COO)Fe	256	quant.	brown	-
37	Ph ₃ Te[{SP(OEt) ₂ }(O ₂ SC ₆ H ₄ Cl-4)N]	oil	84	yellowish	746.67 ^a
38	Ph ₃ Te[(OPPh ₂)(O ₂ SC ₆ H ₄ CH ₃ -4)N]	84	92	colorless	744.7 ^a
39	Ph ₃ Te[(SPPH ₂)(O ₂ SCH ₃)N]	76	74	colorless	752.8 ^a

^a ¹²⁵Te NMR

1. Synthesis of new organochalcogen ligands.

Several diorganochalcogen and diorganodichalcogen ligands were obtained by using the ortho-lithiation route, followed by chalcogen insertion in the C-Li bond. In case of the compounds of type RR'Se lithium bromide is subsequently eliminated, while the R₂Se₂ species were obtained by hydrolysis and oxidation of the lithium organoselenolate. Mainly, several pyrazole based species as well as compounds containing aromatic groups with one or two pendant arms capable for intramolecular coordination were isolated and structurally characterized. Compounds of type R₂E₂ based on diphenyl ether were also the subject of our studies.

The ¹H and ¹³C NMR spectra of the mentioned compounds show characteristic resonances for the organic groups bonded to chalcogen, while the ⁷⁷Se and ¹²⁵Te NMR spectra

show singlet resonances. For the species **1**, **15** and **17** the molecular structures were determined by single-crystal X-ray diffraction and the intramolecular N→Se interaction was evidenced in **1**, while O→E interactions were observed in **15** and **17**.

2. Synthesis of new organo-chalcogen halides of type [2,6-(Me₂NCH₂)C₆H₃]SeX (X = Cl, Br, I)

The organoselenium(II) chloride was obtained by the oxidation of the corresponding diorganodiselenide with sulfuril chloride, while the bromide and the iodide were prepared by reacting the respective chloride with KBr or KI, respectively. Single-crystal X-ray diffraction studies, as well as the molar conductivity for these compounds revealed a ionic structure.

3. Organometallic compounds of group 14 (Sn) and 15 (Bi) elements with organochalcogen ligands.

3.1. Sn(II) complexes

Several of the ligands prepared during this project were used in reactions with tin(II) precursors. The complexes [{2-(Me₂NCH₂)C₆H₄}E]₂Sn (E = S, Se) and [Me₂C(O)CH₂][C₆H₄CH₂NMe₂]E]₂Sn (E = S, Se) were obtained by reactions between diorganodichalcogenides of type [{2-(Me₂NCH₂)C₆H₄}E]₂ or ligands of type [Me₂C(OH)CH₂][C₆H₄CH₂NMe₂]E and Sn[N(SiMe₃)₂]₂ (Scheme 1).



Scheme 1.

Single-crystal X-ray diffraction studies revealed a dimeric structure for compounds **26** and **27** (Figure 1), while for species **28** and **29** a monomeric structure was observed.

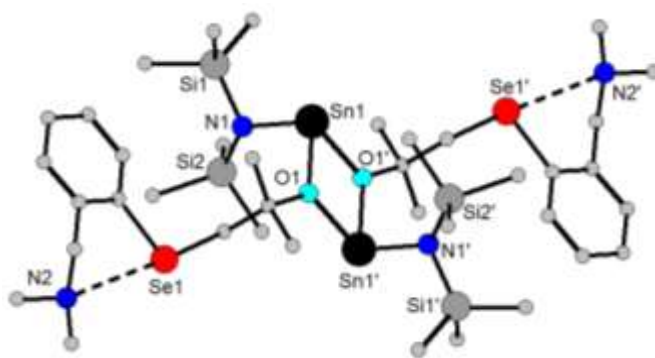


Figure 1. Dimeric association in compound **26**.

The dimeric associations are realized through the oxygen atoms in case of compounds **26** and **27**, while the nitrogen atoms in the pendant arm remain coordinated to chalcogen (Se or S). In case of compounds **28** and **29** the nitrogen atom is interacting with Sn, thus stabilizing in a pseudo-tetrahedral coordination geometry.

3.2. Organotin(IV) hypervalent compounds with ligands containing chalcogen (S, Se) donor atoms

Organotin(IV) compounds with isothio- or isoselenocyanato ligands were prepared by reacting $[2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]_2\text{SnCl}_2$ and alkali metal salts, respectively NH_4SCN or KSeCN . The dithiocarbamates **24** and **25** were also prepared and structurally investigated. The attempts to isolate the species of type $[2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]_2\text{SnCl}(\text{NCE})$ ($\text{E} = \text{S}, \text{Se}$) led to the conclusion that in solution an equilibrium between $[2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]_2\text{SnCl}_2$, $[2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]_2\text{SnCl}(\text{NCS})$ and $[2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]_2\text{Sn}(\text{NCS})_2$ is established, according to the equation given below:



As a consequence, the species $[2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]_2\text{SnCl}(\text{NCE})$ could not be isolated. They were only identified in solution by multinuclear NMR (Figures 2 and 3).

The ^1H NMR spectra suggest the coordination of the nitrogen atom in the pendant arm to tin, while the ^{119}Sn NMR spectra show, by the multiplet aspect due to the $^{14}\text{N} - ^{119}\text{Sn}$ coupling, the coordination of the NCE ligands through nitrogen.

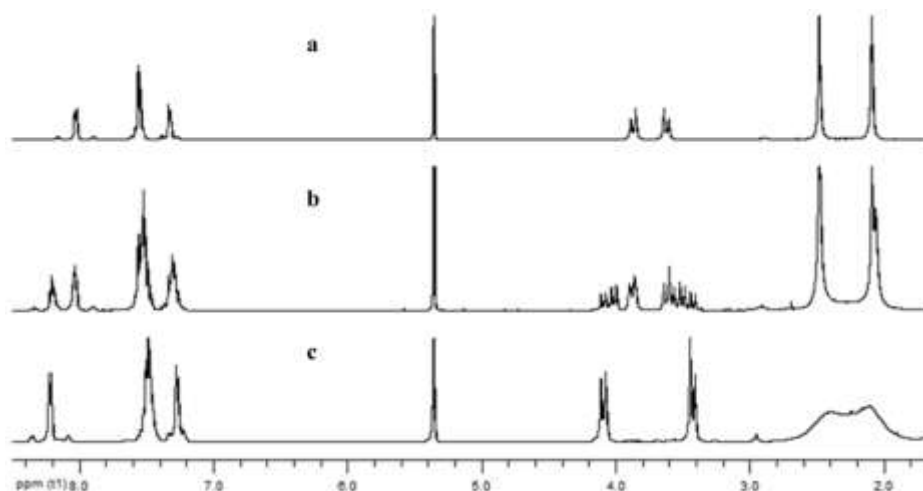


Figure 2. ^1H NMR spectra for $[2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]_2\text{Sn}(\text{NCS})_2$ (**a**), the product isolated in the reaction between $[2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]_2\text{SnCl}_2$ and NH_4SCN in a 1 : 2 molar ratio ($\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$) (**b**) and $[2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]_2\text{SnCl}_2$ (**c**) (CD_2Cl_2 , 400 MHz, 22°C).

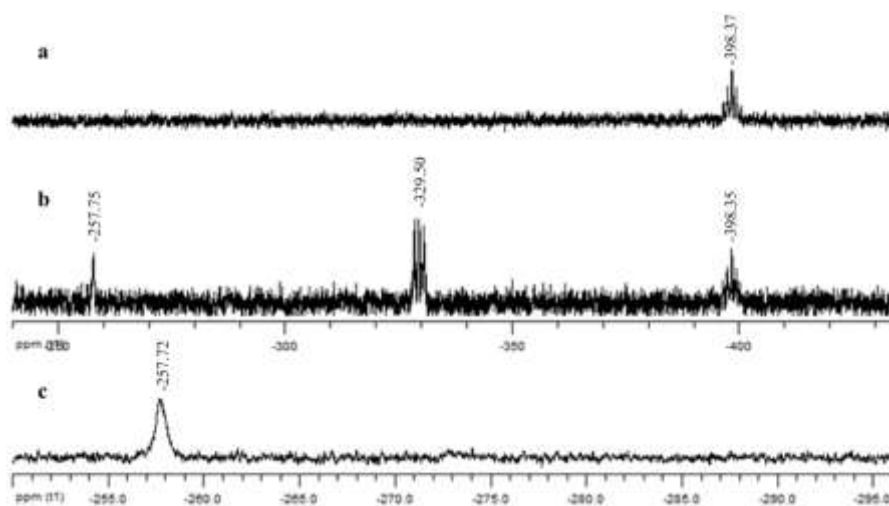


Figure 3. ^{119}Sn NMR spectra for $[2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]_2\text{Sn}(\text{NCS})_2$ (**a**), the product isolated in the reaction between $[2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]_2\text{SnCl}_2$ and NH_4SCN in a 1 : 2 molar ratio ($\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$) (**b**) and $[2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]_2\text{SnCl}_2$ (**c**) (CD_2Cl_2 , 400 MHz, 22°C).

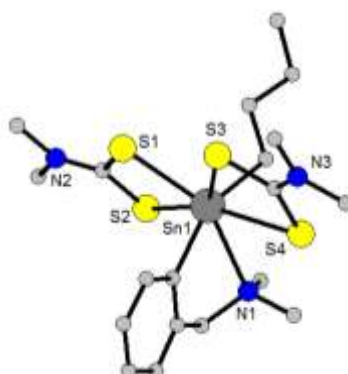


Figure 4. Molecular structure of compound **24**.

For the dithiocarbamato complexes the NMR spectra confirm the equivalence of the dimethyldithiocarbamato (dmdtc) groups in solution. For compound **24** the molecular structure was determined (Figure 4).

3.3. Organobismuth(III) hypervalent compounds with thioether based ligands

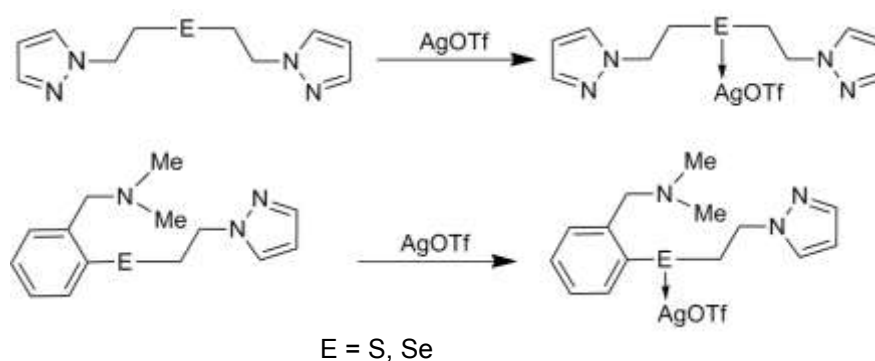
The organoBi(III) compounds belonging to this class were obtained by reacting the starting diphenylthio dibromide with BuLi, followed by LiBr elimination between the later and BiBr₃. By reacting [(C₆H₄CH₂)₂S]BiBr with KI and KNO₃, respectively, were prepared the derivatives **19** and **20**. The isolated species were investigated in solution by ¹H and ¹³C NMR spectroscopy, and in solid state by single-crystal X-ray diffraction. The IR spectrum of compound **20** suggests the bidentate coordination of NO₃⁻ through two of the oxygen atoms.

The single-crystal X-ray diffraction studies evidenced strong π Bi \cdots C_g(Ph centroid) intermolecular interactions.

4. New complexes of *d* metals with organochalcogen ligands

4.1. Complecsi ai metalelor din grupa 11 cu liganzi calcogen-organici

Several silver(I) complexes were obtained by reacting silver salts (AgOTf or AgClO₄) and diorganochalcogen ligands containing pyrazole groups (Scheme 2)



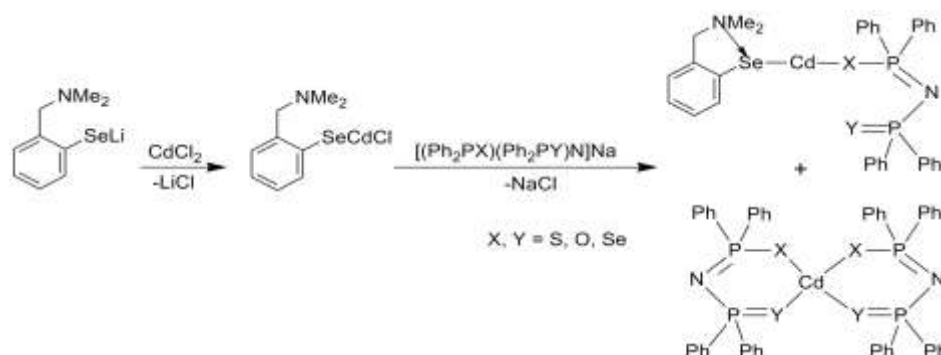
Scheme 2.

The new species were characterized by NMR, MS and IR spectrometry.

Ligands of type [2-(Me₂NCH₂)C₆H₃]⁻ (E = S, Se) were used in order to obtain gold(II) complexes. As gold(I) starting materials were used AuCl or species containing phosphanes as stabilizing agents, such as AuPPh₃, Au₂(dppm) or Au₂(dppe)

4.2. Group 12 metal complexes with organochalcogen ligands

The cadmium(II) species RSeCdCl [$\text{R} = \text{Ph}$, $4\text{-CH}_3\text{C}_6\text{H}_4$, $2\text{-(Me}_2\text{NCH}_2\text{)C}_6\text{H}_4$] were reacted with bidentate organophosphorus ligands, as depicted in Scheme 3.



Scheme 3.

The ^1H and ^{77}Se NMR spectra evidenced the formation of the RSeCdCl species. In Figure 5 are given the ^1H and ^{77}Se NMR spectra ($\delta_{77\text{Se}} = -85$ ppm) for $[2\text{-(Me}_2\text{NCH}_2\text{)C}_6\text{H}_4\text{Se}]\text{CdCl}$. From the reaction with the ligand $[(\text{Ph}_2\text{PSe})_2\text{N}]^-$ a yellow solid was isolated. The NMR spectra suggested the formation of a mixture of compounds, according to Scheme 3.

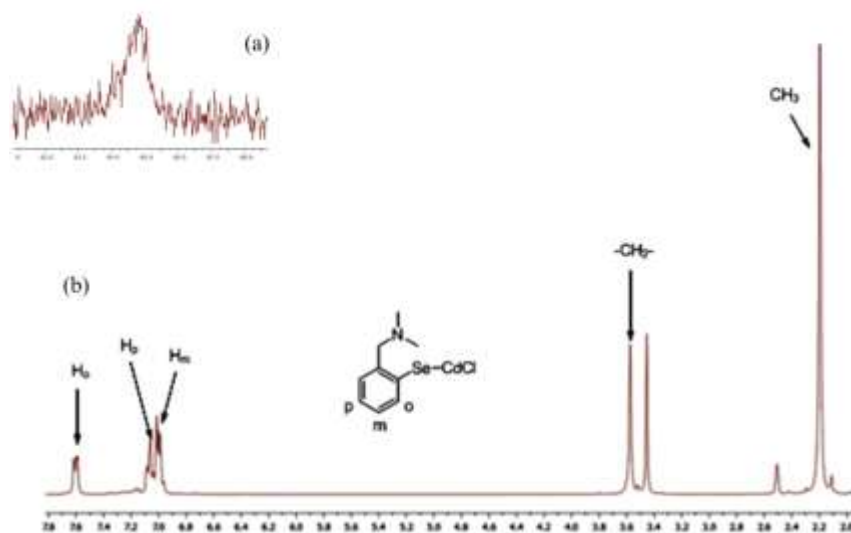


Figure 5. ^{77}Se (a) and ^1H NMR spectra (b) of $[2\text{-(Me}_2\text{NCH}_2\text{)C}_6\text{H}_4\text{Se}]\text{CdCl}$

The attempts to grow single-crystals suitable for X-ray diffraction led to a solid with the molecular structure depicted in Figure 6a. When the ligand $[(\text{Ph}_2\text{PS})(\text{Ph}_2\text{PO})\text{N}]^-$ was used, the isolated species was identified as $[(\text{Ph}_2\text{PS})(\text{Ph}_2\text{PO})\text{N}]_2\text{Cd}$ (Figure 6b).

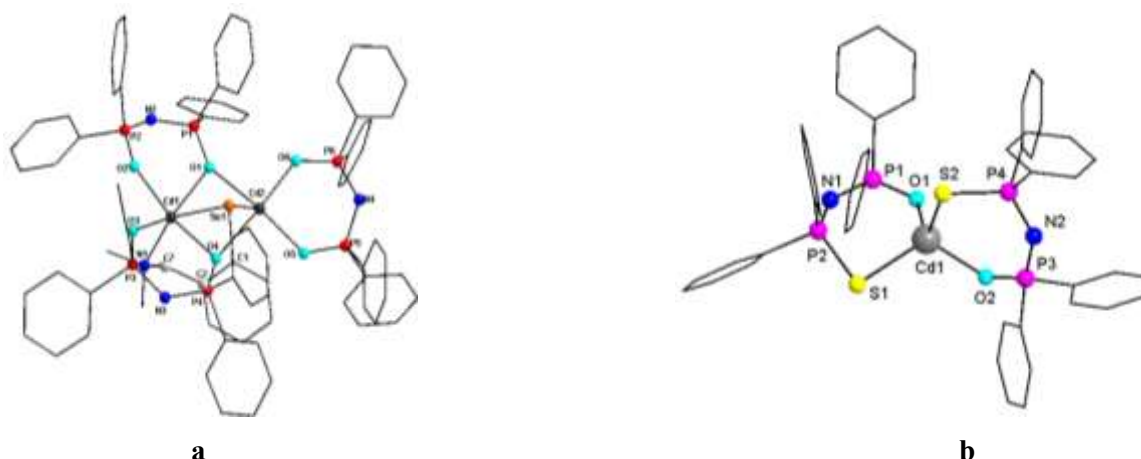


Figure 6.

The low temperature ^{31}P NMR spectra (Figure 7) of the solid product isolated in the reaction between $[2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4\text{Se}]\text{CdCl}$ and $[(\text{Ph}_2\text{PSe})_2\text{N}]\text{K}$ in a 1:1 molar ratio suggests the initial formation of the desired product, which subsequently decomposes in the diorganodiselenide $[2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]_2\text{Se}_2$ and $[(\text{Ph}_2\text{PSe})_2\text{N}]_2\text{Cd}$. These two species seems to react and form the species identified by X-ray diffraction.

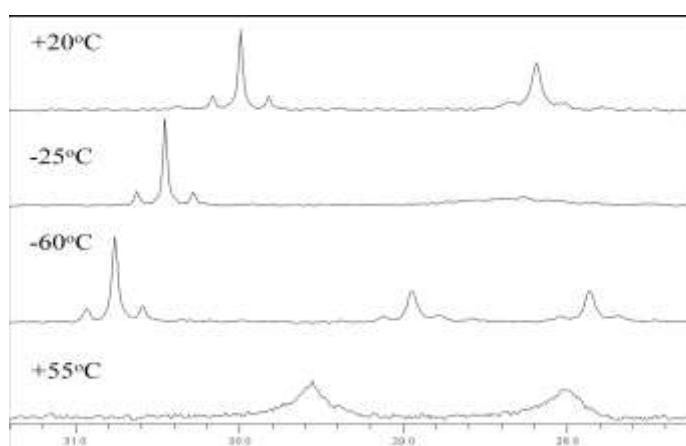
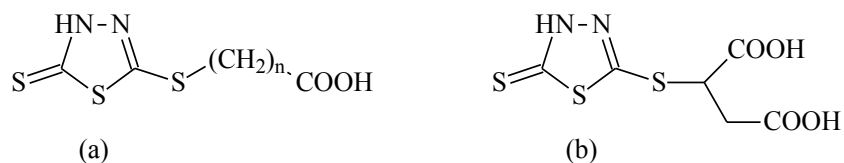


Figure 7. VT ^{31}P NMR spectra of **34**

4.3. Iron(III) and tin(II) complexes with the ligand $[\text{C}_2\text{N}_2\text{S}_3\text{CH}(\text{COO})\text{CH}_2\text{COO}]^-$

Reactions between the acids $\text{C}_2\text{HN}_2\text{S}_3\text{R}$ [$\text{R} = (\text{CH}_2)_2\text{COOH}$ (dmt-d-p) or $\text{CH}(\text{COOH})\text{CH}_2\text{COOH}$ (dmt-d-s) (Scheme 4) with SnCl_2 and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, respectively, in

presence of Et_3N , led to the corresponding complexes, isolated as colorless (Sn) or orange-brown (Fe) solids.



Scheme 4. 2,5-dimercapto-1,3,4-thiadiazole (dmt) (a) and (3H-2-thioxo-1,3,4-thiadiazole-5-yl)-thiosuccinic (b) acids

5. Thermal behavior of the synthesized precursors

Several compounds were investigated by thermogravimetric analysis, in order to establish the decomposition way by increasing the temperature.

The TG curve of the compound $\text{RBU}\text{Sn}(\text{S}_2\text{CNMe}_2)_2$ (Figure 8) revealed its thermal stability until 170 °C. The thermal decomposition of the precursor occurs over a narrow temperature range (170-330°C), when SnS is formed under inert atmosphere. For compound **23** the decomposition proceeds in one step, with formation of solid SnS. In case of the Se containing compounds, the solid residue corresponds to elemental selenium.

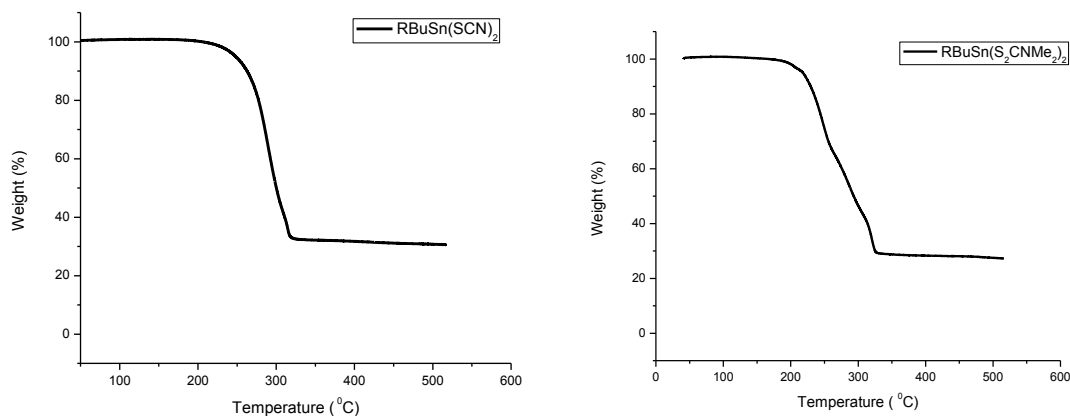


Figure 8. TG curves for compounds **23** and **24**.

The TGA/DTA/DTG curves for the Fe(III) complex $[\text{FeL}] \cdot 1.5\text{H}_2\text{O}$ (Figura 9a) show a decomposition process in 4 steps, with the formation of $\alpha\text{-Fe}_2\text{O}_3$. This process was monitorized by IR spectroscopy and the identity of the final product was established by powder X-ray diffraction (Figura 9b).

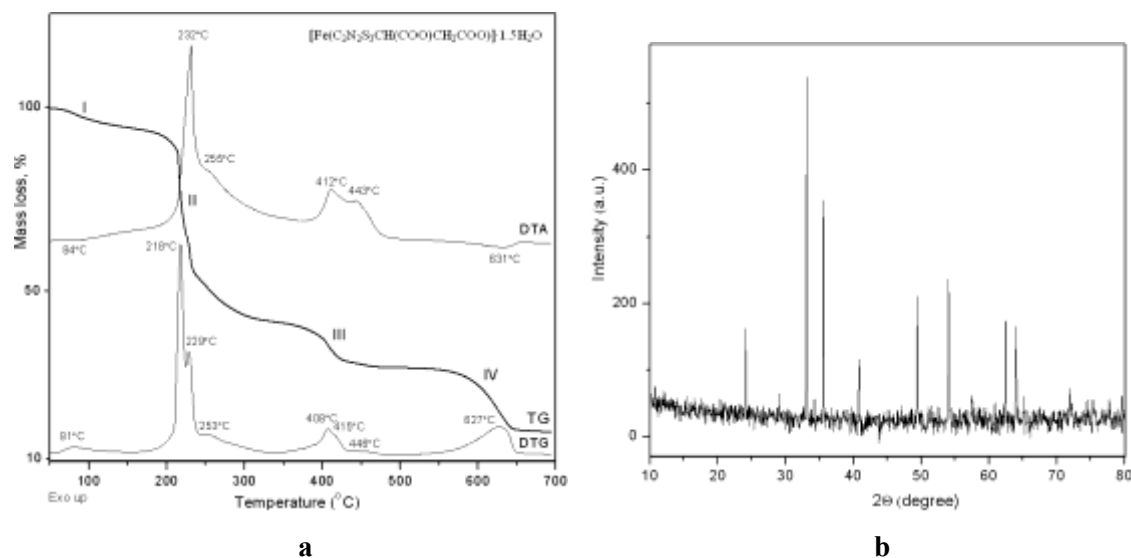


Figure 9. TG/DTA/DTG curves (a) and powder X-ray diffractogram of $[\text{FeL}] \cdot 1.5\text{H}_2\text{O}$ (b)

6. Finalizing step of several studies developed in 2012-2013

Additional studies regarding some compounds obtained in 2012 and 2013 were completed during 2014, as followings: (i) structural characterization and DFT calculations regarding the organoselenium halides containing organic groups with 2 pendant arms, (ii) theoretical analysis by DFT regarding the energies of the conformational isomers of the Zn and Cd complexes with triarylphosphanes of type $[2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]_x\text{Ph}_{3-x}\text{P}$, (iii) reactions between anionic ligands of type $[\{\text{EP}(\text{OEt})_2\}(\text{O}_2\text{SR})\text{N}]$ ($\text{E} = \text{S}, \text{O}$; $\text{R} = \text{C}_6\text{H}_4\text{Cl-4}, \text{C}_6\text{H}_4\text{CH}_3\text{-4}, \text{CH}_3$) and triphenyltelluronium derivatives, (iv) studies regarding the cyclization reactions in oxidation processes of several diorganodichalcogenides.

The new compounds depicted in Table 1 were investigated both in solution and solid state, by NMR and IR spectroscopy and mass spectrometry (ESI or APCI). For some representative species the molecular structure was determined by single-crystal X-ray diffraction.

RESULTS

Published papers, results obtained in 2013

1. New copper(I) complexes with organophosphorus ligands with XPNSO skeleton.
C. Strady, A. Stegarescu, C. Silvestru, A. Silvestru,
Studia Universitatis Babes-Bolyai, Seria Chimia, **2013**, , LVIII, 4, 243-251.

2. Organoselenium(II) halides containing the pincer 2,6-(Me₂NCH₂)₂C₆H₃ ligand – an experimental and theoretical investigation
A. Pop, A. Silvestru, E. J. Juárez-Pérez, M. Arca, V. Lippolis, C. Silvestru,
Dalton Trans., **2014**, 43 (5), 2221 - 2233, DOI: 10.1039/c3dt52886c.
3. Copper(I) complexes with the triarylphosphanes PPh_n(C₆H₄CH₂NMe₂-2)_{3-n} (n = 0-2) and PPh₂[C₆H₄CH₂N(CH₂CH₂)₂O-2]. Synthesis and structural characterization.
A. Covaci, R. Mitea, I. Hosu, A. Silvestru,
Polyhedron, **2014**, 72, 157-163, doi.org/10.1016/j.poly.2014.01.035
4. Diorganochalcogen(II) ligands of type [R₂C(OH)CH₂](2-Me₂NCH₂C₆H₄)E (E = S, Se, Te; R = Me, Ph), and their silver(I) complexes.
A. Pop, R. Mitea, A. Silvestru,
J. Organomet. Chem., **2014**, 768, 121-127. doi.org/10.1016/j.jorganchem.2014.06.007.
5. New diorganodichalcogenides and cyclization reactions leading to 3-benzilamino-benzo[*b*]chalcogenophens.
Alpar Pollnitz, A. Silvestru, *under review*, *Tetrahedron*.
6. Group 12 metal complexes with triarylphosphanes of type PR_xPh_{3-x} [R = 2-(Me₂NCH₂)C₆H₄, 2-{O(CH₂CH₂)₂NCH₂}C₆H₄, x = 1 – 3]
A. Covaci, I. Covaci, A. Silvestru, *under review*, *Dalton Trans.*

Published (or in preparation) papers, results obtained in 2014

7. On the coordination chemistry of organochalcogenolates RNMe₂⁺E⁻ and RNMe₂⁺E⁺O⁻ (E = S, Se) onto lead(II) and lighter divalent tetrel elements.
A. Pop, L. Wang, V. Dorcet, T. Roisnel, J.-F. Carpentier, A. Silvestru, Y. Sarazin,
Dalton Trans., **2014**, 43 (43), 16459 - 16474, DOI: 10.1039/c4dt02252a.
8. Spectroscopic and thermal studies on the iron(III) mercapto-thiadiazol-thiosuccinate precursor for iron(III) oxides
M. M. Venter, V. N. Bercean, F. Goga, M. Nasui, *in press*, *Rev. Roum. Chim.*, 59 (11-12) 2014.
9. New triphenyltelluronium salts of organophosphorus ligands.
N. Chiorean, D. Margineanu, A. Silvestru, *in press*, *Rev. Roum. Chim.*, 59 (11-12) 2014.
10. Cadmium organoselenolates and their behaviour towards organophosphorus ligands.
A. Toma, R. Suteu, A. Silvestru, *manuscript in preparation*, *Inorg. Chim. Acta*.
11. Diorganodichalcogenides based on diphenylether groups and their chemical reactivity.
A. Toma, T. Ruffer, M. Mehring, A. Silvestru, *manuscript in preparation*, *Journal of Organometallic Chemistry*.
12. Organotin(IV) compounds with dithioato ligands. Synthesis, structure and thermal behaviour.
C. Coza, A. Stegarescu, A. Silvestru, *manuscript in preparation*, *Applied Organometallic Chemistry*.
13. Hypervalent organoselenium ligands and their group 11 metal complexes.
R. Popa, A. Silvestru, A. Pop, *manuscript in preparation*, *Journal of Organometallic Chemistry*.

Conferences 2014

1. Hypervalent organometallic compounds with relevance for nanomaterials and biology.
Anca Silvestru,
invited lecture at 13th Academic Days, Timișoara, June 2014.

2. Organotellurium compounds - potential precursors for nanomaterials.
Nora Chiorean, Eleonora Denes, Anca Silvestru,
poster presentation at 13th Academic Days, Timișoara, June 2014.
3. New hypervalent tin(IV) pseudo-halides. Synthesis and structural characterization.
C. Coza, A. Stegarescu, A. Silvestru,
poster presentation la A XXXIII-a Conferință Națională de Chimie, Căciulata, oct. 2014.
4. Organoselenium compounds with *NCN* pincer ligands. Structure and chemical behavior.
A. Pop, R. Popa, A. Silvestru,
poster presentation la EUCHEMS, Istanbul, aug. 2014.
5. Thermal decomposition studies on iron(III) mercapto-thiadiazol-thiocarboxylato precursor for iron-based materials
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Director de proiect,

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